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(54) [Title of the Invention] Optical Recording Medium

(57) [Abstract] An optical recording medium comprised of a transparent substrate on which a light absorbing layer including an organic dye, a light reflecting layer, and a protective layer are successively stacked, said optical recording medium characterized in that the light reflecting layer is mainly comprised of silver and includes 0.1 to 5 atomic% of at least one type of element selected from the group comprised of rhodium, palladium, platinum, titanium, molybdenum, tantalum, zirconium, vanadium, and tungsten.

[Effects] To enable production of a high reliability optical recording medium excellent in high temperature and high humidity resistance at a low cost.

[CLAIMS]

[Claim 1] An optical recording medium comprised of a transparent substrate on which a light absorbing layer including an organic dye, a light reflecting layer, and a protective layer are successively stacked, said optical recording medium characterized in that the light reflecting layer is mainly comprised of silver and includes 0.1 to 5 atomic% of at least one type of element selected from the group comprised of rhodium, palladium, platinum, titanium, molybdenum, tantalum, zirconium, vanadium, and tungsten.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Field of Utilization in Industry] The present invention relates to an optical recording medium. More particularly, it relates to a writable optical disk which is interchangeable with a so-called compact disk (CD).

[0002]

[Prior Art] Compact disks have been widely used in the past as media for audio software, computer game software, and electronic publishing due to their large storage capacity and high productivity as software packages. However, in order to produce compact disks, dies for transferring recordings to their transparent substrates are necessary. The cost per disk ends up becoming considerably high when producing less than a 100 or so disks due to the die costs.

[0003] In order to solve this problem, rather than produce recording disks through dies, compact disks provided with recordable areas enabling direct recording on the disk, i.e., recordable compact disks, are being developed. Recordable compact disks can be recorded on and exhibit similar reflectivities as read only compact disks, so have the advantage that they can be played back by read only compact disk players and drives after recording.

[0004] This recordable compact disk is usually produced by successively providing a transparent substrate with a light absorbing layer including an organic dye, a light reflecting layer which consists of a metal, and a protective layer which consists of a UV curing resin.

[0005]

[Problem(s) to be Solved by the Invention] In the recordable compact disks already commercialized and marketed, in order to obtain a 65% or more high reflectivity with respect to the wavelength of the read laser light and a high corrosion resistance, gold and alloys comprised mainly of gold are being used the light reflecting layers. Gold, however, is expensive, so this is becoming a major problem in terms of costs.

[0006] On the other hand, when using silver, copper, aluminum, or another metal which is inexpensive, but has high reflectivity on a par with gold or alloys mainly comprised of the same as the light reflecting layer, a drop in reflectivity due to corrosion of the light reflecting layer or a change in the disk characteristics such as the error rate easily occur, so it was difficult to produce recordable compact disks with sufficient reliability for the usage environment.

[0007] On the other hand, the use of corrosion resistant alloys such as stainless steel has been proposed to improve the corrosion resistance, but most of these call for large amounts of additive ingredients for exhibiting the corrosion resistance, so the reflectivity of the alloy becomes low. Moreover, since an anticorrosion mechanism forms a passive film on the surface of the alloy, when used as a reflective film, a decline in reflectivity was unavoidable.

[0008]

[Means for Solving the Problem] The present invention has as its object to solve the above problems in the prior art and provide a low cost optical disk suitable for a recordable

compact disk by making it possible to use a cheaper metal as the light reflecting layer while maintaining a lifetime and reliability equivalent to those of a recordable optical disk using high corrosion resistance gold as a light reflecting layer.

[0009] Usually, in a recordable compact disk, the light reflecting layer is formed on top of it with a protective layer, so the light reflecting layer is not exposed to an extreme metal corrosive environment. Therefore, there is no meaning in imparting endurance to acidic, alkaline, oxidizing, or reducing substances more than required and it is possible to reduce the amounts of additive elements. Therefore, the present inventors engaged in intensive studies on metals having high reflectivities and combinations of fine amounts of additive elements effectively imparting corrosion resistance to them in order to overcome the above problems. As a result, they discovered that by using a light reflecting layer comprised mainly of silver and including 0.1 to 5 atomic% of at least one type of element selected from the group of rhodium, palladium, platinum, titanium, molybdenum, tantalum, zirconium, vanadium, and tungsten, an optical recording medium with a high reflectivity and little decline in reflectively over time can be obtained and therefore perfected the present invention.

[0010] Namely, the gist of the present invention lies in an optical recording medium comprised of a transparent substrate on which a light absorbing layer including an organic dye, a light reflecting layer, and a protective layer are successively stacked, said optical recording medium characterized in that the light reflecting layer is mainly comprised of silver and includes 0.1 to 5 atomic% of at least one type of element selected from the group comprised of rhodium, palladium, platinum, titanium, molybdenum, tantalum,

zirconium, vanadium, and tungsten.

[0011] Below, the optical recording medium of the present invention will be explained in detail. The optical recording medium of the present invention comes comprises a transparent substrate on the surface of which are successive stacked a light absorbing layer, a light reflecting layer comprised of silver or mainly of silver, and a protective layer. As the material of the transparent substrate, a polycarbonate, polymethyl methacrylate, an amorphous polyolefin, or other plastic or glass may be mentioned. The transparent substrate used has a thickness of about 1 to 2 mm and is formed with a guide groove in a spiral.

[0012] As the material of the light absorbing layer, organic dyes such as a cyanine dye, squarylium dye, croconium dye, azulenium dye, triarylamine dye, anthraquinone dye, metal-containing azo dye, dithiol metallic complex dye, India aniline metal complex dye, phthalocyanine dye, naphthalocyanine dye, intermolecular CT dye, etc. are suitable. These are used alone or mixed or in the form with the addition of an antidegradant, binder, etc.

[0013] As the method of forming the light absorbing layer containing an organic dye, the method of dissolving the organic dye in an organic solvent and spin coating it on the transparent substrate directly or through another layer is used preferably, but it is also possible to use vapor deposition for a dye having sublimability like a phthalocyanine dye. The thickness of the light absorbing layer is suitably selected according to the wavelength to be used, the optical constant of the reflecting layer, the material of the light absorbing layer, etc. in consideration of the recording sensitivity, performance coefficient, etc. for the power of the laser light or other recording light and is usually in the range of 100Å to 5 μm. The light absorbing layer may be provided on both sides of

the transparent substrate or may be provided on one side.

[0014] For the light reflecting layer, use is made of a metal thin film of an alloy mainly comprised of silver and containing at least one type of element selected from the group comprised of rhodium, palladium, platinum, titanium, molybdenum, tantalum, zirconium, vanadium, and tungsten. By this, the corrosion resistance is improved compared with the case where silver is used alone. As the ingredient of the additive element, rhodium is the most effective, followed by palladium, platinum, and titanium, but it is possible to select a suitable additive element from the ones listed above according to the material of the adjoining light absorbing layer. The amount of the additive element is in total 0.1 to 5 atomic%, more preferably 0.1 to 3 atomic%. The composition can be confirmed easily by fluorescent X-ray analysis. The light reflecting layer is suitably formed on the light absorbing layer directly or through another layer by sputtering or vapor deposition to make a 50 to 200 nm thick polycrystalline film.

[0015] Furthermore, in accordance with need, the surface of the light reflecting layer may be treated by a triazine thiol compound or other surface treatment agent. As the protective layer formed on the light reflecting layer, use of hard material such as an acrylic UV curing resin etc. is preferred. Usually, this is formed by coating the light reflecting layer directly or through another layer by spin coating to a thickness of 2 to 20 μm, then curing by irradiation of UV rays.

[0016]

[Examples] Below, the present invention will be explained in more detail with reference to examples and comparative examples, but the present invention is not limited to the following examples insofar as its gist is not exceeded.

Example 1

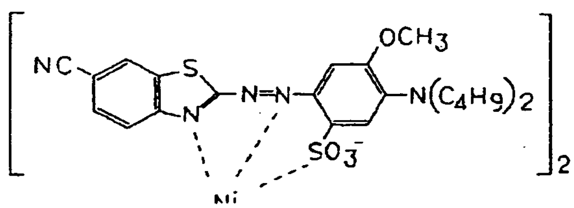
As a transparent substrate, use was made of a polycarbonate

substrate with a diameter of 120 mm and a thickness of 1.2 mm provided with a spiral tracking groove for use for recordable compact disks.

[0017] The light absorbing layer was fored by the method of dissolving the metal-containing azo dye shown by the structural formula (1) in an amount of 2.2 wt% (with respect to the weight of the solvent) in methyl cellusolve, filtering it, then spin coating it on the above substrate. After coating the dye layer, the assembly was dried in an 80°C oven for 10 minutes to cause the solvent in the dye layer to completely evaporate away. The thickness of the dye layer was selected so that the reflectivity might become high and was made 120 nm.

[0018]

[Formula 1]



.... ①

[0019] Subsequently, the light absorbing layer was formed with, as a light reflecting layer, a silver-rhodium alloy (rhodium content: two atomic%) to a thickness of 100 nm by DC magnetron sputtering in argon gas. Furthermore, the light reflecting layer was coated with the UV curing agent SD-318 (made by Dainippon Ink and Chemicals) by spin coaing to a thickness of 3 μm. This was irradiated by UV rays by a UV ray irradiation device to cure the coating and form a protective layer.

[0020] The resultant recordable compact disk was recorded on by an EFM signal by an optical disk evaluation apparatus DDU-1000 (made by Pulsetech) and was measured for the change of reflectivity and C1 error (average of number of errors

occurring per second) before and after a 500 hour high temperature and high humidity test under conditions of a temperature of 85°C and a humidity of 85%, whereupon just a slight decline in reflectivity and increase in C1 error were seen. The results are shown in Table 1.

Example 2

Except for using as the light reflecting layer a 100 nm thick silver-titanium-molybdenum alloy (titanium content: 1.8 atomic%, molybdenum content: 0.2 atomic%), the same procedure was followed as in Example 1 to produce a recordable compact disk.

[0021] When testing the obtained disk in the same way as in Example 1, only a slight decline in reflectivity and increase in C1 error were seen. The results are shown in Table 1.

Example 3

Except for using as the light reflecting layer a 100 nm thick silver-palladium-tungsten alloy (palladium content: 2.8 atomic%, tungsten content: 0.2 atomic%), the same procedure was followed as in Example 1 to produce a recordable compact disk.

[0022] When testing the obtained disk in the same way as in Example 1, only a slight decline in reflectivity and increase in C1 error were seen. The results are shown in Table 1.

Example 4

Except for using as the light reflecting layer a 100 nm thick silver-platinum-molybdenum alloy (platinum content: 4.7 atomic%, molybdenum content: 0.3 atomic%), the same procedure was followed as in Example 1 to produce a recordable compact disk.

[0023] When testing the obtained disk in the same way as in Example 1, only a slight decline in reflectivity and increase in C1 error were seen. The results are shown in Table 1.

Example 5

Example 8

Except for using as the light reflecting layer a 100 nm thick silver-palladium-zirconium alloy (palladium content: 3.5 atomic%, zirconium content: 0.5 atomic%), the same procedure was followed as in Example 3 to produce a recordable compact disk.

[0028] When testing the obtained disk in the same way as in Example 1, only a slight decline in reflectivity and increase in C1 error were seen. The results are shown in Table 1.

Example 9

Except for using as the light reflecting layer a 100 nm thick silver-titanium-vanadium alloy (titanium content: 1.2 atomic%, vanadium content: 0.1 atomic%), the same procedure was followed as in Example 3 to produce a recordable compact disk.

[0029] When testing the obtained disk in the same way as in Example 1, only a slight decline in reflectivity and increase in C1 error were seen. The results are shown in Table 1.

Comparative Example 1

Except for using as the light reflecting layer silver (purity 99.99%), the same procedure was followed as in Example 1 to produce a recordable compact disk.

[0030] When testing the obtained disk in the same way as in Example 1, a decline in reflectivity and huge increase in C1 error were seen. The results are shown in Table 1.

Comparative Example 2

Except for using as the light reflecting layer silver (purity 99.99%), the same procedure was followed as in Example 3 to produce a recordable compact disk.

[0031] When testing the obtained disk in the same way as in Example 1, the reflectivity was less than 65% and a huge increase in C1 error was seen. The results are shown in Table 1.

Comparative Example 3

Except for using as the light reflecting layer a 100 nm thick silver-rhodium alloy (rhodium content: 4.5 atomic%), the same procedure was followed as in Example 3 to produce a recordable compact disk.

[0032] When testing the obtained disk in the same way as in Example 1, almost no change was seen in both the reflectivity and C1 error, but the reflectivity was less than 65% or not satisfying the characteristics reuqired for CD interchangeability. The results are shown in Table 1. [0033]

[Table 1]

	Reflectivity		C1 error	
	Before test	After test	Before test	After test
Ex. 1	70	69	3	8
Ex. 2	69	68	2	12
Ex. 3	68	67	3	9
Ex. 4	66	66	3	6
Ex. 5	71	69	3	10
Ex. 6	71	67	2	18
Ex. 7	69	67	4	11
Ex. 8	67	66	3	9
Ex. 9	70	69	2	20
Comp. Ex. 1	71	66	3	247
Comp. Ex. 2	69	64	3	359
Comp. Ex. 3	62	62	4	5

The following is clear from Table 1.

[0034] In Comparative Example 1 and Comparative Example 2, declines in reflectivity and huge increases in C1 error are seen due to corrosion of the light reflecting layers. As opposed to this, in Examples 1 to 3 applying the present invention,

even after a high temperature and high humidity test, it was learned that the decline in reflectivity and the increase in C1 error became small. On the other hand, when adding rhodium exceeding 5 atomic%, while the decline in reflectivity and the increase in C1 error are suppressed, it is learned that the 65% reflectivity required for CD interchangeability is not reached.

[0035]

[Effect of the Invention] According to the present invention, a high reliability optical recording medium excellent in high temperature and high humidity resistance can be produced at a low cost, so the invention is extremely advantageous for industry.

[Voluntary Amendment]

[Date] 22.2.2000

[Voluntary Amendment 1]

[Name of Document to be Amended] Specification

[Name of Item to be Amended] Claims

[Method of Amendment] Change

[Content of Amendment]

[CLAIMS]

[Claim 1] An optical recording medium comprised of a transparent substrate on which a light absorbing layer including an organic dye, a light reflecting layer, and a protective layer are successively stacked, said optical recording medium characterized in that the light reflecting layer is mainly comprised of silver and includes 0.1 to 5 atomic% of at least one type of element selected from the group comprised of rhodium, palladium, platinum, titanium, molybdenum, tantalum, zirconium, vanadium, and tungsten.

[Claim 2] An optical recording medium as set forth in claim 1, wherein the light reflecting layer is comprised mainly of silver and contains 0.1 to 5 atomic% of at least one element selected from the group comprising rhodium, palladium, platinum, and titanium.

[Claim 3] An optical recording medium as set forth in claim 1 or 2, wherein the light reflecting layer is a polycrystalline layer.